Supporting Information

For

**A General and Practical Method of Alkynyl Indole
and Benzofuran Synthesis via Tandem Cu and
Pd-Catalyzed Cross Couplings**

Masatoshi Nagamochi, Yuan-Qing Fang and Mark Lautens*

*Davenport Research Laboratories, Department of Chemistry, University of Toronto
80 St. George Street, Toronto, Ontario, M5S 3H6, Canada
mlautens@chem.utoronto.ca*

Table of Contents

Experimental Procedures	S3
General	S3
Synthesis of Indoles	S4
Synthesis of Benzofurans	S15
Supporting Spectra (in numerical order)	S26

General All the reactions were carried out under argon or nitrogen. Glassware was oven dried. Solvents and solutions were added with a syringe. Analytical Thin Layer Chromatography was performed using Silicycle normal phase 0.25 mm aluminium-backed plates and visualization was accomplished with 250 nm UV light. Column chromatography was carried out as “flash chromatography” as reported by Still¹ using SilicycleTM Ultra-Pure 230-400 mesh silica gel.

All reagents, metal catalysts and ligands were obtained from commercial sources without further purification. Toluene was distilled under nitrogen from sodium/benzophenone immediately prior to use. Dichloromethane and dichloroethane were distilled under nitrogen from CaH₂. MeOH and DMF were purchased from Aldrich and use without further distillation.

Melting points were taken on a Fisher-Johns melting point apparatus without correction. IR spectra were obtained using Nicolet DX FT IR spectrometer as a chloroform solution with NaCl cellule. High-resolution mass spectra were obtained from a VG 70-250S (double focusing) mass spectrometer at 70 eV. ¹H and ¹³C NMR spectra were obtained using Varian Mercury 400 or Mercury 300 spectrometers. Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; quint, quintuplet; m, multiplet and br, broad peak. ¹H spectra were referenced to tetramethylsilane (TMS, 0 ppm) using CDCl₃ or DMSO-*d*₆ as the solvent; ¹³C spectra were referenced to solvent carbons (77.0 ppm for CDCl₃).

¹ Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

Synthesis of Indoles

I. Starting Materials (1)²

[2-(2,2-Dibromovinyl)phenyl]methylamine (1g)

To a solution of [2-(2,2-dibromovinyl)phenyl]amine (1.15 g, 4.15 mmol), formaldehyde (37 wt. % solution in H₂O, 400 mg), acetic acid (0.5 mL) in dichloroethane (3 mL) and MeOH (3 mL) was added sodium triacetoxyborohydride (1.10 g, 5.19 mmol) at 0 °C, and the mixture was stirred for 24 h at rt. The solvent was removed *in vacuo* and the resultant crude material was dissolved with EtOAc (50 mL) and sat. NaHCO₃ (20 mL). The mixture was extracted with EtOAc (2 × 50 mL), and the combined organic layers were washed with brine, dried over MgSO₄, filtered and then concentrated *in vacuo*. The resulting material was purified by flash chromatography eluting with 3%–5% EtOAc in hexane to give **1g** as a pale yellow oil (495 mg, 41%). IR (CHCl₃) ν 3418, 2913, 2815, 1602, 1520, 1316, 1259, 1166 cm⁻¹; ¹H-NMR (CDCl₃) δ : 7.31–7.23 (3H, m), 6.73 (1H, dt, *J* = 7.6, 0.9 Hz), 6.64 (1H, d, *J* = 8.5 Hz), 3.65 (1H, br s), 2.87 (3H, s); ¹³C NMR (75 MHz, CDCl₃) δ 146.2, 134.3, 130.1, 129.3, 121.7, 116.9, 110.3, 93.2, 30.8; HRMS (EI) *m/z* *calcd.* for: [M]⁺ 288.9102, *m/z* *found*: 288.9103

II. Indoles (2)

2-Phenylethynyl-1H-indole (2a)

To a 10 mL round-bottomed flask was charged with 10% Pd-C (26.6 mg, 0.025 mmol) and PPh₃ (14.4 mg, 0.055 mmol), and the flask was purged with argon for at least 10 min. To the second separate flask was charged with *ortho-gem*-dibromovinylaniline (0.139 g, 0.5 mmol), CuI (4.8 mg, 0.025 mmol), and the flask was purged with argon for

² More details about the starting material preparation not described here, see the Supporting Information: Fang, Y.-Q.; Lautens, M. *Org. Lett.* **2005**, 7, 3549.

10 min, followed by addition of toluene (5 mL), phenylacetylene (82 μ L, 0.75 mmol), and $i\text{Pr}_2\text{NH}$ (174 μ L, 1.25 mmol). After the mixture in the second flask became homogenous, it was cannulated into the first flask, and the resulting mixture was heated at 100 $^\circ\text{C}$ for 1 h. The mixture was diluted with Et_2O (30 mL), washed with H_2O (20 mL), brine (15 mL), and dried over MgSO_4 . The crude material after removal of solvent was purified by flash chromatography using 5 $\rightarrow$ 10% EtOAc in hexane to give **2a** as a pale yellow solid (0.088 g, 85%). mp: 161-162 $^\circ\text{C}$. IR (neat, cm^{-1}): 3384, 3052, 2213, 1596, 1482, 1442, 1398, 1353, 1308, 1235, 1104. ^1H NMR (300 MHz, CDCl_3) δ 8.22 (1H, br), 7.60 (1H, d, $J = 7.9$ Hz), 7.56-7.52 (2H, m), 7.37-7.32 (4H, m), 7.24 (1H, ddd, $J = 7.6, 7.6, 1.0$ Hz), 7.13 (1H, ddd, $J = 7.5, 7.5, 0.9$ Hz), 6.84 (1H, d, $J = 1.6$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 136.4, 131.7, 128.8, 128.0, 123.8, 122.8, 121.1, 120.7, 119.0, 110.9, 109.1, 92.8, 82.0.

2-Oct-1-ynyl-1H-indole (2b)

To a tube (24 $\times$ 150 mm) of Carousel reaction station was charged with *ortho-gem*-dibromovinylaniline (139 mg, 0.50 mmol), 10% Pd-C (10.6 mg, 0.010 mmol, 2 mol%), $\text{P}(p\text{-MeOPh})_3$ (14.1 mg, 0.040 mmol, 8 mol%), and CuI (3.8 mg, 0.020 mmol, 4 mol%), and the tube was evacuated and purged with argon three times followed by addition of toluene (3 mL, degassed), $i\text{Pr}_2\text{NH}$ (175 μ L, 1.25 mmol), and 1-octyne (110 μ L, 0.75 mmol). The reaction mixture was heated to 100 $^\circ\text{C}$ for 1.5 h. H_2O (10 mL) was added, and the mixture was extracted with EtOAc (2 $\times$ 15 mL), and dried over MgSO_4 . The crude material after removal of solvent was purified by flash chromatography using 3% EtOAc in hexane to afford **2b** as a pale yellow oil (93.5 mg, 83%). IR (neat, cm^{-1}) 3410, 2931, 2858, 2231, 1453, 1349, 1296, 1145. ^1H NMR (300 MHz, CDCl_3) δ 8.07 (1H, br), 7.55 (1H, d, $J = 7.9$ Hz), 7.26 (1H, d, $J = 8.0$ Hz), 7.19 (1H, $J = 7.6, 7.6, 0.9$ Hz), 7.09 (1H, ddd, $J = 7.4, 7.4, 1.2$ Hz), 6.65 (1H, m), 2.44 (2H, t, $J = 7.1$ Hz), 1.66-1.56 (2H, m), 1.49-1.41 (2H, m), 1.34-1.28 (4H, m), 0.91 (3H, t, $J = 6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 135.9, 128.0, 123.1, 120.7, 120.4, 119.8, 110.7, 107.6, 94.1, 73.2, 31.6, 28.8, 28.7, 22.7, 19.8, 14.3. HRMS (ESI) calc'd for $\text{C}_{16}\text{H}_{19}\text{N}$ ($[\text{M}]^+$): 225.1518. Found: 225.1517.

5-(1*H*-Indol-2-yl)-pent-4-yn-1-ol (**2c**)

To a 10 mL round-bottomed flask was charged with 10% Pd-C (26.6 mg, 0.025 mmol) and PPh₃ (14.4 mg, 0.055 mmol), and the flask was purged with argon for at least 10 min. To the second separate flask was charged with *ortho-gem*-dibromovinylaniline (0.139 g, 0.5 mmol), CuI (4.8 mg, 0.025 mmol), and the flask was purged with argon for 10 min, followed by addition of toluene (5 mL), pent-4-yn-1-ol (69 μ L, 0.75 mmol), and *i*Pr₂NH (174 μ L, 1.25 mmol). After the mixture in the second flask became homogenous, it was cannulated into the first flask, and the resulting mixture was heated at 100 °C for 1 h. The mixture was diluted with Et₂O (30 mL), washed with H₂O (20 mL), brine (15 mL), and dried over MgSO₄. The crude material was purified by flash chromatography using 3.5→5% EtOAc in hexane to afford **2c** as a pale yellow oil (0.065 g, 65%). IR (neat, cm⁻¹): 3541, 3396, 2948, 2233, 1451, 1350, 1296, 1046. ¹H NMR (300 MHz, CDCl₃) δ 8.35 (1H, br), 7.55 (1H, d, *J* = 7.9 Hz), 7.25 (1H, d, *J* = 8.1 Hz), 7.18 (1H, *J* = 7.6, 7.6, 1.1 Hz), 7.09 (1H, ddd, *J* = 7.5, 7.5, 0.9 Hz), 6.65 (1H, d, *J* = 1.5 Hz), 3.80 (2H, t, *J* = 5.3 Hz), 2.56 (2H, t, *J* = 7.0 Hz), 1.97 (1H, br), 1.85 (2H, quintet, *J* = 6.5 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 136.0, 127.9, 123.2, 120.8, 120.4, 119.4, 110.9, 107.7, 92.9, 73.8, 61.8, 31.3, 16.3. HRMS (EI) calc'd for C₁₃H₁₃NO ([M]⁺): 199.0997. Found: 199.0995.

2-[5-(Tetrahydropyran-2-yloxy)-pent-1-ynyl]-1*H*-indole (**2d**)

To a 10 mL round-bottomed flask was charged with 10% Pd-C (26.6 mg, 0.025 mmol) and PPh₃ (14.4 mg, 0.055 mmol), and the flask was purged with argon for at least 10 min. To the second separate flask was charged with *ortho-gem*-dibromovinylaniline (0.139 g, 0.5 mmol), CuI (4.8 mg, 0.025 mmol), and the flask was purged with argon for 10 min, followed by addition of toluene (5 mL), 2-pent-4-ynyloxytetrahydropyran (0.115 g, 0.676 mmol), and *i*Pr₂NH (174 μ L, 1.25 mmol). After the mixture in the second flask became homogenous, it was cannulated into the first flask, and the resulting mixture was heated at 100 °C for 1 h. The crude material was purified by flash chromatography using 15→20% EtOAc in hexanes to afford **2d** as a slightly yellow oil (0.105 g, 71%). IR (neat, cm⁻¹): 3406, 3283, 2944, 2870, 2244, 1452, 1350, 1296, 1137, 1119, 1033. ¹H NMR (300 MHz, CDCl₃) δ 8.27 (1H, br), 7.55 (1H, d, *J* = 7.8 Hz), 7.28

(1H, d, $J = 8.1$ Hz), 7.19 (1H, $J = 7.5, 7.5, 0.9$ Hz), 7.09 (1H, t, $J = 7.6$ Hz), 6.64 (1H, d, $J = 1.8$ Hz), 4.65 (1H, t, $J = 3.4$ Hz), 3.95-3.88 (2H, m), 3.59-3.50 (2H, m), 2.58 (2H, t, $J = 7.1$ Hz), 1.96-1.70 (4H, m), 1.63-1.54 (4H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 135.9, 127.9, 123.1, 120.8, 120.4, 119.6, 110.8, 107.6, 99.1, 93.2, 73.6, 66.1, 62.5, 30.9, 28.9, 25.7, 19.7, 16.7. HRMS (EI) calc'd for $\text{C}_{18}\text{H}_{21}\text{NO}_2$ ($[\text{M}]^+$): 283.1572. Found: 283.1572.

3-(1H-Indol-2-yl)prop-2-yn-1-ol (2e)

A carousel reaction tube (24×150 mm) was charged with 2-(2,2-Dibromovinyl)aniline (120 mg, 0.43 mmol), 10% Pd-C (9.2 mg, 0.0087 mmol, 2 mol%), $\text{P}(p\text{-MeOPh})_3$ (12.0 mg, 0.034 mmol, 8 mol%), and CuI (3.9 mg, 0.020 mmol, 4 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (3 mL, degassed), $i\text{Pr}_2\text{NH}$ (157 μL , 1.12 mmol) and propargyl alcohol (0.30 mL, 5.2 mmol), and then heated to 100 °C with stirring for 12 h. The reaction mixture was then cooled to rt and H_2O (10 mL) added. The mixture was extracted with EtOAc (2×15 mL), and combined extracts were washed with sat. NH_4Cl and brine, then dried and solvent was removed *in vacuo*. The resulting crude material was purified by flash chromatography eluting with 50–60% EtOAc in hexane to afford **2e** as a pale brown solid (29.6 mg, 40%). mp: 49–51 °C; IR (CHCl_3) ν 3398, 2923, 2228, 1450, 1403, 1350, 1299, 1229, 1038, 1012 cm^{-1} ; ^1H -NMR (CDCl_3) δ : 8.19 (1H, s), 7.58 (1H, d, $J = 7.6$ Hz), 7.19–7.19 (2H, m), 7.12 (1H, t, $J = 7.3$ Hz), 6.76 (1H, br s), 4.54 (2H, s), 1.82 (1H, br s); ^{13}C NMR (75 MHz, CDCl_3) δ 127.7, 123.9, 121.1, 120.7, 111.0, 109.3, 90.8, 51.8; HRMS (EI) m/z calcd. for: $[\text{M}]^+$ 171.0684, m/z found: 171.0682.

2-Trimethylsilanylethynyl-1H-indole (2f)

A carousel reaction tube (24×150 mm) was charged with 2-(2,2-dibromovinyl)aniline (139 mg, 0.50 mmol), 10% Pd-C (10.6 mg, 0.01 mmol, 2 mol%), $\text{P}(p\text{-OMeP})_3$ (14.2 mg, 0.040 mmol, 8 mol%), and CuI (3.8 mg, 0.020 mmol, 4 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (3 mL, degassed), $i\text{Pr}_2\text{NH}$ (175 μL , 1.25 mmol) and trimethylsilylacetylene (0.71 mL, 5.0 mmol), and then heated to 100 °C with stirring for 12 h. The reaction mixture was then cooled to rt and H_2O (10 mL) added. The mixture was extracted with EtOAc (2×15 mL), and combined extracts were washed with sat. NH_4Cl and brine, then dried and solvent was removed *in*

vacuo. The resulting crude material was purified by flash chromatography eluting with 10% EtOAc in hexane to afford **2f** as a pale brown solid (61.0 mg, 57%). mp: 91-92 °C; IR (CHCl₃) ν 3402, 2961, 2157, 1398, 1343, 1249 cm⁻¹; ¹H-NMR (CDCl₃) δ : 8.16 (1H, br s), 7.57 (1H, d, J = 7.9 Hz), 7.29 (1H, dd, J = 7.9, 1.2 Hz), 7.22 (1H, td, J = 7.9, 1.2 Hz), 7.11 (2H, td, J = 7.9, 1.2 Hz), 6.77 (1H, d, J = 1.2 Hz), 0.27 (9H, s); ¹³C NMR (75 MHz, CDCl₃) δ 135.8, 127.4, 123.6, 120.9, 120.4, 118.5, 110.6, 109.2, 98.3, 96.8, -0.20; HRMS (EI) m/z calcd. for: [M]⁺ 213.0974, m/z found: 213.0974.

6-(1*H*-Indol-2-yl)hex-5-ynenitrile (**2g**)

A carousel reaction tube (24×150 mm) was charged with 2-(2,2-dibromovinyl)aniline (139 mg, 0.50 mmol), 10% Pd-C (10.6 mg, 0.0087 mmol, 2 mol%), P(*p*-MeOPh)₃ (14.1 mg, 0.040 mmol, 8 mol%), and CuI (3.9 mg, 0.020 mmol, 4 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (3 mL, degassed), *i*Pr₂NH (180 μ L, 1.28 mmol) and 5-hexynenitrile (80 μ L, 0.75 mmol), and then heated to 100 °C with stirring for 24 h. The reaction mixture was then cooled to rt and H₂O (10 mL) added. The mixture was extracted with EtOAc (2 × 15 mL), and combined extracts were washed with sat. NH₄Cl and brine, then dried and solvent was removed *in vacuo*. The resulting crude material was purified by flash chromatography eluting with 25% EtOAc in hexane to afford **2g** as a pale brown oil (52.3 mg, 50%). IR (CHCl₃) ν 3390, 2358, 1995, 1350, 1295 cm⁻¹; ¹H-NMR (CDCl₃) δ : 8.23 (1H, s), 7.56 (1H, d, J = 7.9 Hz), 7.33-7.07 (3H, m), 6.68 (1H, br s), 2.65 (2H, t, J = 6.7 Hz), 2.56 (2H, t, J = 7.0 Hz), 2.03-1.92 (2H, m); ¹³C NMR (75 MHz, CDCl₃) δ 136.0, 127.8, 123.5, 120.9, 120.6, 119.4, 118.8, 110.9, 108.2, 90.6, 75.2, 24.5, 19.0, 16.5; HRMS (EI) m/z calcd. for: [M]⁺ 208.1000, m/z found: 208.0996.

2-(6-Chlorohex-1-ynyl)-1*H*-indole (**2h**)

A carousel reaction tube (24×150 mm) was charged with 2-(2,2-dibromovinyl)aniline (139 mg, 0.50 mmol), 10% Pd-C (10.6 mg, 0.0087 mmol, 2 mol%), P(*p*-MeOPh)₃ (12.0 mg, 0.034 mmol, 8 mol%), and CuI (3.9 mg, 0.020 mmol, 4 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (3 mL, degassed),

*i*Pr₂NH (175 μ L, 1.25 mmol) and 6-chloro-1-hexyne (80 μ L, 0.75 mmol), and then heated to 100 $^{\circ}$ C with stirring for 48 h. The reaction mixture was then cooled to rt and H₂O (10 mL) added. The mixture was extracted with EtOAc (2 $\times$ 15 mL), and combined extracts were washed with sat. NH₄Cl and brine, then dried and solvent was removed *in vacuo*. The resulting crude material was purified by flash chromatography eluting with 15% EtOAc in hexane to afford **2h** as a pale yellow oil (81.3 mg, 70%). IR (CHCl₃) ν 3405, 2950, 1615, 1538, 1451, 1349, 1295 cm⁻¹; ¹H-NMR (CDCl₃) δ : 8.08 (1H, s), 7.55 (1H, d, *J* = 7.9 Hz), 7.33-7.05 (3H, m), 6.66 (1H, d, *J* = 1.5 Hz), 3.60 (2H, t, *J* = 6.4 Hz), 2.50 (2H, t, *J* = 6.9 Hz), 2.02-1.71 (4H, m); ¹³C NMR (75 MHz, CDCl₃) δ 135.9, 127.9, 123.3, 120.8, 120.5, 119.4, 110.8, 107.9, 93.0, 73.8, 44.7, 31.9, 25.9, 19.1; HRMS (ESI) *m/z* calcd. for: [M+H]⁺ 232.0890, *m/z* found: 232.0887.

2-Pyridin-3-ylethynyl-1H-indole (2i)

A carousel reaction tube (24 $\times$ 150 mm) was charged with 2-(2,2-dibromovinyl)aniline (139 mg, 0.50 mmol), 10% Pd-C (10.6 mg, 0.010 mmol, 2 mol%), P(*p*-MeOPh)₃ (14.1 mg, 0.040 mmol, 8 mol%), and CuI (3.8 mg, 0.020 mmol, 4 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (3 mL, degassed), *i*Pr₂NH (175 μ L, 1.25 mmol) and 3-ethynylpyridine (80.0 mg, 0.77 mmol), and then heated to 100 $^{\circ}$ C with stirring for 12 h. The reaction mixture was then cooled to rt and H₂O (10 mL) added. The mixture was extracted with EtOAc (2 $\times$ 15 mL), and combined extracts were washed with sat. NH₄Cl and brine, then dried and solvent was removed *in vacuo*. The resulting crude material was purified by flash chromatography eluting with 40% EtOAc in hexane to afford **2i** as a white solid (88.0 mg, 81%). mp: 209-211 $^{\circ}$ C; IR (CHCl₃) ν 3403, 2157, 1652, 1558, 1539, 1506, 1457, 1249 cm⁻¹; ¹H-NMR (CDCl₃) δ : 8.83 (1H, s), 8.60 (1H, s), 7.83 (1H, dt, *J* = 8.1, 1.8 Hz), 7.63 (1H, d, *J* = 8.1 Hz), 7.41-7.22 (4H, m), 7.19-7.10 (1H, m), 6.89 (1H, dd, *J* = 2.1, 0.9 Hz); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 152.0, 149.7, 139.0, 137.2, 127.7, 124.4, 123.9, 121.2, 120.6, 119.8, 118.1, 112.0, 109.0, 89.2, 86.5; HRMS (EI) *m/z* calcd. for: [M]⁺ 218.0844, *m/z* found: 218.0846.

2-Oct-1-ynyl-1H-benzo[g]indole (2j)

A carousel reaction tube (24×150 mm) was charged with 2-(2,2-dibromovinyl)naphthalen-1-ylamine (110 mg, 0.34 mmol), 10% Pd-C (7.1 mg, 0.0066 mmol, 2 mol%), P(*p*-MeOPh)₃ (4.6 mg, 0.013 mmol, 4 mol%), and CuI (2.8 mg, 0.0066 mmol, 2 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (3 mL, degassed), *i*Pr₂NH (120 μL, 0.84 mmol) and 1-octyne (80 μL, 0.54 mmol), and then heated to 100 °C with stirring for 12 h. The reaction mixture was then cooled to rt and H₂O (10 mL) added. The mixture was extracted with EtOAc (2 × 15 mL), and combined extracts were washed with sat. NH₄Cl and brine, then dried and solvent was removed *in vacuo*. The resulting crude material was purified by flash chromatography eluting with 15% EtOAc in hexane to afford **2j** as a pale brown solid (51.0 mg, 55%). mp: 90-91 °C; IR (CHCl₃) ν 3414, 2930, 1519, 1393 cm⁻¹; ¹H-NMR (CDCl₃) δ : 8.83 (1H, s), 7.85-7.85 (2H, m), 7.61 (1H, d, *J* = 8.8 Hz), 7.54-7.37 (3H, m), 6.78 (1H, d, *J* = 2.1 Hz), 2.48 (2H, t, *J* = 7.0 Hz), 1.72-1.23 (8H, m), 0.92 (3H, t, *J* = 6.7 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 131.0, 130.6, 129.1, 125.8, 124.4, 124.0, 121.5, 121.4, 120.6, 119.7, 118.0, 109.2, 93.9, 73.2, 31.6, 28.9, 28.8, 22.8, 19.8, 14.3; HRMS (EI) *m/z* calcd. for: [M]⁺ 275.1674, *m/z* found: 275.1679.

4-Benzyloxy-5-methoxy-2-oct-1-ynyl-1H-indole (2k)

A carousel reaction tube (24×150 mm) was charged with 3-benzyloxy-2-(2,2-dibromovinyl)-4-methoxyphenylamine (136 mg, 0.33 mmol), 10% Pd-C (7.0 mg, 0.0066 mmol, 2 mol%), P(*p*-MeOPh)₃ (4.6 mg, 0.013 mmol, 4 mol%), and CuI (1.3 mg, 0.0063 mmol, 2 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (3 mL, degassed), *i*Pr₂NH (140 μL, 1.0 mmol) and 1-octyne (118 μL, 0.85 mmol), and then heated to 100 °C with stirring for 12 h. The reaction mixture was then cooled to rt and H₂O (10 mL) added. The mixture was extracted with EtOAc (2 × 15 mL), and combined extracts were washed with sat. NH₄Cl and brine, then dried and solvent was removed *in vacuo*. The resulting crude

material was purified by flash chromatography eluting with 5% EtOAc in hexane to afford **2k** as a colorless oil (96.0 mg, 81%). IR (CHCl₃) ν 3334, 3031, 2930, 2857, 1583, 1504, 1463, 1454, 1428, 1331, 1282, 1245, 1174, 1093 cm⁻¹; ¹H-NMR (CDCl₃) δ : 7.98 (1H, s), 7.55-7.48 (2H, m), 7.41-7.27 (3H, m), 6.94 (2H, t, J = 9.4 Hz), 6.69 (1H, d, J = 2.1 Hz), 5.21 (2H, s), 3.87 (3H, s), 2.43 (2H, t, J = 7.0 Hz), 1.67-1.24 (8H, m), 0.91 (3H, t, J = 6.9 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 145.5, 140.8, 138.4, 133.0, 128.5, 128.2, 127.9, 123.4, 120.1, 113.3, 105.9, 105.1, 94.1, 75.2, 73.0, 58.6, 31.5, 28.8, 28.7, 22.7, 19.7, 14.2; HRMS (EI) m/z calcd. for: [M]⁺ 361.2042, m/z found: 361.2046.

4-Fluoro-2-oct-1-ynyl-1H-indole (2l)

A carousel reaction tube (24×150 mm) was charged with 2-(2,2-dibromovinyl)-3-fluorophenylamine (150 mg, 0.51 mmol), 10% Pd-C (10.6 mg, 0.010 mmol, 2 mol%), P(*p*-MeOPh)₃ (7.1 mg, 0.020 mmol, 4 mol%), and CuI (2.0 mg, 0.010 mmol, 2 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (3 mL, degassed), *i*Pr₂NH (180 μ L, 1.25 mmol) and 1-octyne (110 μ L, 0.75 mmol), and then heated to 100 °C with stirring for 24 h. The reaction mixture was then cooled to rt and H₂O (10 mL) added. The mixture was extracted with EtOAc (2 × 15 mL), and combined extracts were washed with sat. NH₄Cl and brine, then dried and solvent was removed *in vacuo*. The resulting crude material was purified by flash chromatography eluting with 5% EtOAc in hexane to afford **2l** as a pale yellow oil (88.0 mg, 72%). IR (CHCl₃) ν 3412, 2925, 2856, 1582, 1534, 1507, 1351, 1237, 1168, 1036 cm⁻¹; ¹H-NMR (CDCl₃) δ : 8.15 (1H, s), 7.15-7.02 (2H, m), 6.80-6.69 (2H, m), 2.44 (2H, t, J = 7.0 Hz), 1.68-1.24 (8H, m), 0.91 (3H, t, J = 6.9 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 156.1 (J_{CF} = 246.0 Hz), 138.1 (J_{CF} = 10.5 Hz), 123.6 (J_{CF} = 7.5 Hz), 119.9, 117.2, 106.8 (J_{CF} = 3.8 Hz), 105.1 (J_{CF} = 18.8 Hz), 103.5, 94.5, 72.6, 31.5, 28.8, 28.6, 22.7, 19.7, 14.2; HRMS (ESI) m/z calcd. for: [M+H]⁺ 244.1495, m/z found: 244.1496.

2-Oct-1-ynyl-1H-indole-5-carboxylic acid methyl ester (2m)

A carousel reaction tube (24×150 mm) was charged with 4-amino-3-(2,2-dibromovinyl)benzoic acid methyl ester (110 mg, 0.33 mmol), 10% Pd-C (17.5 mg, 0.017 mmol, 5 mol%), P(*p*-MeOPh)₃ (9.2 mg, 0.026 mmol, 8 mol%),

and CuI (2.7 mg, 0.014 mmol, 4 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (3 mL, degassed), *i*Pr₂NH (140 μ L, 1.00 mmol) and 1-octynyne (80 μ L, 0.54 mmol), and then heated to 100 °C with stirring for 24 h. The reaction mixture was then cooled to rt and H₂O (10 mL) added. The mixture was extracted with EtOAc (2 $\times$ 15 mL), and combined extracts were washed with sat. NH₄Cl and brine, then dried and solvent was removed *in vacuo*. The resulting crude material was purified by flash chromatography eluting with 10% EtOAc in hexane to afford **2m** as a pale brown solid (78.1 mg, 84%). mp: 87-88 °C; IR (CHCl₃) ν 3317, 2931, 2857, 1694, 1615, 1538, 1435, 1347, 1315, 1259, 1156 cm⁻¹; ¹H-NMR (CDCl₃) δ : 8.42-8.30 (2H, m), 7.90 (1H, dd, *J* = 8.6, 1.8 Hz), 7.29 (1H, d, *J* = 8.6 Hz), 6.72 (1H, s), 3.92 (3H, s), 2.44 (2H, t, *J* = 7.0 Hz), 1.22-1.22 (8H, m), 0.91 (3H, t, *J* = 6.9 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 168.2, 138.4, 127.6, 124.5, 123.7, 122.6, 121.3, 110.4, 108.6, 95.1, 72.5, 52.0, 31.5, 28.8, 28.6, 22.7, 19.7, 14.2; HRMS (EI) *m/z* calcd. for: [M]⁺ 283.1572, *m/z* found: 283.1577.

1-Methyl-2-oct-1-ynyl-1H-indole (2n)

A carousel reaction tube (24 $\times$ 150 mm) was charged with [2-(2,2-dibromovinyl)phenyl]methylaniline (130 mg, 0.45 mmol), 10% Pd-C (14.2 mg, 0.013 mmol, 3 mol%), P(*p*-MeOPh)₃ (6.3 mg, 0.018 mmol, 4 mol%), and CuI (1.7 mg, 0.0089 mmol, 2 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (3 mL, degassed), *i*Pr₂NH (190 μ L, 1.34 mmol) and 1-octynyne (100 μ L, 0.67 mmol), and then heated to 100 °C with stirring for 24 h. The reaction mixture was then cooled to rt and H₂O (10 mL) added. The mixture was extracted with EtOAc (2 $\times$ 15 mL), and combined extracts were washed with sat. NH₄Cl and brine, then dried and solvent was removed *in vacuo*. The resulting crude material was purified by flash chromatography eluting with 1%–3% EtOAc in hexane to afford **2n** as a pale yellow oil (65.1 mg, 61%). IR (CHCl₃) ν 2928, 2856, 1462, 1385, 1340, 1313, 1237 cm⁻¹; ¹H-NMR (CDCl₃) δ : 7.54 (1H, dt, *J* = 7.9, 1.0 Hz), 7.27-7.18 (2H, m), 7.12-7.05 (1H, m), 6.65 (1H, s), 3.77 (3H, s), 2.50 (2H, t, *J* = 7.0 Hz), 1.71-1.59 (2H, m), 1.55-1.26 (6H, m), 0.91 (3H, t, *J* = 7.0 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 136.8, 127.2, 122.9, 122.4, 120.6, 119.8, 109.2, 106.0, 96.6, 72.2, 31.3, 30.4, 28.6(2C), 22.5, 19.6, 14.0; HRMS (EI) *m/z* calcd. for: [M]⁺ 239.1674, *m/z* found: 239.1678.

1-Isopropyl-2-oct-1-ynyl-1H-indole (2o)

A carousel reaction tube (24×150 mm) was charged with [2-(2,2-dibromovinyl)phenyl]isopropylamine (160 mg, 0.50 mmol), 10% Pd-C (26.5 mg, 0.025 mmol, 5 mol%), P(*p*-MeOPh)₃ (14.1 mg, 0.040 mmol, 8 mol%), and CuI (6.0 mg, 0.020 mmol, 4 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (3 mL, degassed), *i*Pr₂NH (210 μL, 1.49 mmol) and 1-octynye (110 μL, 0.75 mmol), and then heated to 100 °C with stirring for 24 h. The reaction mixture was then cooled to rt and H₂O (10 mL) added. The mixture was extracted with EtOAc (2 × 15 mL), and combined extracts were washed with sat. NH₄Cl and brine, then dried and solvent was removed *in vacuo*. The resulting crude material was purified by flash chromatography eluting 2.5% EtOAc in hexane to afford **2o** as a pale yellow oil (80.0 mg, 60%). IR (CHCl₃) ν 2929, 2856, 2361, 2340, 1454, 1408, 1352, 1313, 1192 cm⁻¹; ¹H-NMR (CDCl₃) δ : 7.54 (1H, d, *J* = 7.9 Hz), 7.42 (1H, d, *J* = 8.5 Hz), 7.21-7.13 (1H, m), 7.10-7.02 (1H, m), 6.65 (1H, s), 5.04-4.88 (1H, m), 2.49 (2H, t, *J* = 7.0 Hz), 1.70-1.28 (8H, m), 1.64 (6H, d, *J* = 7.0 Hz), 0.91 (3H, t, *J* = 6.9 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 135.2, 128.1, 122.1, 121.7, 121.0, 119.6, 110.8, 107.5, 96.9, 73.3, 48.3, 31.5, 28.8, 28.7, 22.8, 21.8, 19.9, 14.2; HRMS (EI) *m/z* calcd. for: [M]⁺ 267.1987, *m/z* found: 267.1987.

1-Benzyl-2-oct-1-ynyl-1H-indole (2p)

A carousel reaction tube (24×150 mm) was charged with Benzyl[2-(2,2-dibromovinyl)phenyl]amine (120 mg, 0.33 mmol), 10% Pd-C (23.7 mg, 0.022 mmol, 7 mol%), P(*p*-MeOPh)₃ (11.2 mg, 0.033 mmol, 10 mol%), and CuI (6.0 mg, 0.033 mmol, 10 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (3 mL, degassed), *i*Pr₂NH (115 μL, 0.82 mmol) and 1-octynye (72 μL, 0.49 mmol), and then heated to 100 °C with stirring for 24 h. The reaction mixture was then cooled to rt and H₂O (10 mL) added. The mixture was extracted with EtOAc (2 × 15 mL), and combined extracts were washed with sat. NH₄Cl and brine, then dried and solvent was removed *in vacuo*. The resulting crude material

was purified by flash chromatography eluting with 2.5% EtOAc in hexane to afford **2p** as a pale yellow solid (52.6 mg, 51%). mp: 43-44 °C; IR (CHCl₃) ν 3029, 2927, 2855, 1454, 1391, 1345, 1312, 1161 cm⁻¹; ¹H-NMR (CDCl₃) δ : 7.58-7.54 (1H, m), 7.34-7.04 (8H, m), 6.73 (1H, s), 5.41 (2H, s), 2.44 (2H, t, J = 7.0 Hz), 1.62-1.23 (8H, m), 0.87 (3H, t, J = 6.5 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 138.1, 136.5, 128.8, 127.8, 127.5, 126.9, 122.8, 120.9, 120.3, 110.1, 106.8, 97.1, 72.5, 48.0, 31.5, 28.8, 28.7, 22.7, 19.9, 14.2; HRMS (EI) m/z calcd. for: [M]⁺ 315.1987, m/z found: 315.1981.

2-Oct-1-ynyl-1-phenyl-1H-indole (2q)

A carousel reaction tube (24×150 mm) was charged with [2-(2,2-dibromovinyl)phenyl]phenylamine (130 mg, 0.37 mmol), 10% Pd-C (3.9 mg, 0.0037 mmol, 1 mol%), P(*p*-MeOPh)₃ (5.2 mg, 0.015 mmol, 4 mol%), and CuI (1.4 mg, 0.0074 mmol, 2 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (3 mL, degassed), *i*Pr₂NH (134 μ L, 0.97 mmol) and 1-octyne (81 μ L, 0.55 mmol), and then heated to 100 °C with stirring for 24 h. The reaction mixture was then cooled to rt and H₂O (10 mL) added. The mixture was extracted with EtOAc (2 × 15 mL), and combined extracts were washed with sat. NH₄Cl and brine, then dried and solvent was removed *in vacuo*. The resulting crude material was purified by flash chromatography eluting with 2% EtOAc in hexane to afford **2q** as a colorless oil (72.1 mg, 65%). IR (CHCl₃) ν 3057, 2928, 2854, 1596, 1499, 1449, 1377, 1360, 1330, 1314, 1241, 1201, 1144 cm⁻¹; ¹H-NMR (CDCl₃) δ : 7.63-7.37 (6H, m), 7.24-7.09 (3H, m), 6.82 (1H, s), 2.32 (2H, t, J = 7.0 Hz), 1.39-1.39 (2H, m), 1.15-1.14 (6H, m), 0.87 (3H, t, J = 6.9 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 138.0, 137.3, 129.3, 129.1, 127.8, 127.6, 127.5, 123.2, 122.9, 120.8, 110.6, 108.4, 96.9, 72.8, 31.5, 28.6, 28.4, 22.7, 19.7, 14.3; HRMS (EI) m/z calcd. for: [M]⁺ 301.1831, m/z found: 301.1834.

Synthesis of Benzofurans

I. Starting Materials (3)

3-(2,2-Dibromovinyl)-4-hydroxybenzoic acid methyl ester (3b)

To a solution of methyl 3-formyl-4-hydroxybenzoate (900 mg, 5.0 mmol) and 2,6-lutidine (0.93 ml, 8.0 mmol) in CH_2Cl_2 (11 mL) was added *tert*-butyldimethylsilyl trifluoromethanesulfonate (1.5 mL, 6.5 mmol) at 0 °C, and the mixture was stirred for 3 h at rt. Sat. NaHCO_3 (10 mL) was added, and the resulting mixture was extracted with CH_2Cl_2 (2 $\times$ 30 mL). The combined extracts were washed with brine, dried (MgSO_4) and solvent removed under reduced pressure. The residue was purified by flash chromatography eluting with 10% 15% EtOAc in hexane to afford methyl 4-*tert*-butyldimethylsilyloxy-3-formylbenzoate as a white solid (1.18 g, 81%). mp: 52-53 °C; IR (CHCl_3) ν 2952, 1725, 1692, 1607, 1491, 1272, 1118 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ : 10.46 (1H, s), 8.50 (1H, d, J = 2.3 Hz), 8.14 (1H, dd, J = 8.8, 2.3 Hz), 6.93 (1H, d, J = 8.8 Hz), 3.91 (3H, s), 1.03 (9H, s), 0.32 (6H, s); ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ 193.5, 170.2, 166.5, 140.9, 134.9, 131.0, 127.8, 124.3, 56.4, 29.9 (3C), 22.6, 0.0 (2C); HRMS (EI) m/z *calcd.* for: $[\text{M}-t\text{Bu}]^+$ 237.0583, m/z *found*: 237.0581.

To a solution of methyl 4-*tert*-butyldimethylsilyloxy-3-formylbenzoate (500 mg, 1.70 mmol) in CH_2Cl_2 (50 mL) was added carbon tetrabromide (5.56 g, 16.8 mmol) and triphenylphosphine (8.78 g, 33.5 mmol) at 0 °C, and the mixture was stirred for 15 h at rt. 1M $\text{Na}_2\text{S}_2\text{O}_3$ (30 mL) was added, and the resulting mixture was extracted with CH_2Cl_2 (2 $\times$ 120 mL). The combined extracts were washed with sat. NaHCO_3 , H_2O and brine, then dried (MgSO_4) and solvent removed under reduced pressure. The residue was purified by flash chromatography eluting with 5% EtOAc in hexane to afford 4-(*tert*-Butyldimethylsilyloxy)-3-(2,2-dibromovinyl)benzoic acid methyl ester as a colorless oil (660 mg, 86%). IR (CHCl_3) ν 2953, 2858, 1732, 1605, 1488, 1286, 1116, 998 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ : 8.36-8.33 (1H, m), 7.91 (1H, dd, J = 8.5, 2.1 Hz), 7.56 (1H, s), 6.81 (1H, d, J = 8.5 Hz), 3.89 (3H, s), 1.02 (9H, s), 0.24 (6H, s); ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ 170.8, 161.4, 137.4, 135.7, 135.6, 131.7, 127.4, 123.4, 95.6, 56.4, 30.0, 29.9, 22.5, 0.0; HRMS (EI) m/z *calcd.* for: $[\text{M}]^+$ 448.9792, m/z *found*: 448.9777.

To a solution of 4-(*tert*-Butyldimethylsilyloxy)-3-(2,2-dibromovinyl)benzoic acid methyl ester (600 mg, 1.32 mmol) in THF (45 mL) was added TBAF (2.0 mL, 2.0 mmol) at 0 °C, and the mixture was stirred for 3 h at rt. Water (20 mL) was added, and the resulting mixture was extracted with EtOAc (2 $\times$ 100 mL). The combined extracts

were washed with sat. NH_4Cl and brine, then dried (MgSO_4) and solvent was removed under reduced pressure. The residue was purified by flash chromatography eluting with 10%–30% EtOAc in hexane to afford **3b** as a white solid (365 mg, 82%). mp: 199–200 °C; IR (CHCl_3) ν 3411, 1770, 1683, 1652, 1270 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ : 8.40 (1H, d, $J = 2.1$ Hz), 8.10 (1H, dd, $J = 8.4, 2.1$ Hz), 7.68 (1H, s), 7.03 (1H, d, $J = 8.4$ Hz), 5.61 (1H, s), 4.06 (3H, s); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ 166.3, 159.8, 133.0, 132.0, 130.9, 122.9, 120.7, 116.2, 91.1, 52.5; HRMS (EI) m/z *calcd. for*: $[\text{M}]^+$ 334.8929, m/z *found*: 334.8912.

1-(2,2-Dibromovinyl)naphthalen-2-ol (**3c**)

To a solution of 2-hydroxy-1-naphthaldehyde (3.0 g, 17.4 mmol) and Et_3N (4.9 mL, 35 mmol) in CH_2Cl_2 (50 mL) was added *tert*-butyldimethylsilyl trifluoromethanesulfonate (5.2 mL, 22.6 mmol) at 0 °C, and the mixture was stirred for 3 h at rt. Sat. NaHCO_3 (30 mL) was added, and the resulting mixture was extracted with CH_2Cl_2 (2×100 mL). The combined extracts were washed with brine, dried (MgSO_4) and solvent removed under reduced pressure. The residue was purified by flash chromatography eluting with 10% EtOAc in hexane to afford 2-(*tert*-butyldimethylsilyloxy)naphthalene-1-carbaldehyde as a colorless oil (4.6 g, 93%). IR (CHCl_3) ν 2928, 1673, 1632, 1592, 1507, 1463, 1435, 1314, 1245, 1155, 1012 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ : 10.87 (1H, s), 9.28 (1H, d, $J = 8.8$ Hz), 7.95 (1H, d, $J = 9.1$ Hz), 7.76 (1H, d, $J = 7.3$ Hz), 7.65–7.57 (1H, m), 7.46–7.39 (1H, m), 7.06 (1H, d, $J = 8.8$ Hz), 1.05 (9H, s), 0.32 (6H, t, $J = 3.2$ Hz); ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ 196.4, 165.6, 141.1, 135.8, 133.6, 133.0, 132.2, 129.0 (2C), 124.7, 123.2, 29.7, 22.5, 0.0; HRMS (EI) m/z *calcd. for*: $[\text{M}]^+$ 287.1467, m/z *found*: 287.1465.

To a solution of 2-(*tert*-butyldimethylsilyloxy)naphthalene-1-carbaldehyde (3.2 g, 11.2 mmol) in CH_2Cl_2 (50 mL) was added carbon tetrabromide (5.56 g, 16.8 mmol) and triphenylphosphine (8.78 g, 33.5 mmol) at 0 °C, and the mixture was stirred for 12 h at rt. 1M $\text{Na}_2\text{S}_2\text{O}_3$ (30 mL) was added, and the resulting mixture was extracted with CH_2Cl_2 (2×120 mL). The combined extracts were washed with sat. NaHCO_3 , H_2O and brine, then dried (MgSO_4) and solvent removed under reduced pressure. The residue was purified by flash chromatography eluting with 2% EtOAc in hexane to afford *tert*-butyl-[1-(2,2-dibromovinyl)naphthalen-2-yloxy]dimethylsilane as a colorless oil (4.05 g, 82%). IR (CHCl_3) ν 3062, 2955, 2928, 2857, 1592, 1505, 1471, 1463, 1429, 1377, 1338, 1282, 1250, 1143, 1075 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) δ : 7.56–7.48 (3H, m), 7.37 (1H, s), 7.25 (1H, t, $J = 6.7$ Hz), 7.11 (1H, t, $J = 8.2$ Hz), 6.83 (1H, d, $J = 8.8$ Hz), 0.82

(9H, s), 0.00 (6H, s); ^{13}C NMR (75 MHz, DMSO- d_6) δ 154.4, 138.1, 135.5, 134.0, 133.2 (2C), 130.7, 128.5, 128.0, 125.8, 124.9, 98.4, 81.5, 81.0, 80.6, 29.8, 22.2, 0.0; HRMS (EI) m/z calcd. for: $[\text{M}]^+$ 439.9823, m/z found: 439.9807.

To a solution of *tert*-butyl-[1-(2,2-dibromovinyl)naphthalen-2-yloxy]dimethylsilane (3.7 g, 8.3 mmol) in THF (45 mL) was added TBAF (11.7 mL, 11.7 mmol) at 0 °C, and the mixture was stirred for 2 h at rt. Water (20 mL) was added, and the resulting mixture was extracted with EtOAc (2 $\times$ 100 mL). The combined extracts were washed with sat. NH_4Cl and brine, then dried (MgSO_4) and solvent was removed under reduced pressure. The residue was purified by flash chromatography eluting with 20%–25% EtOAc in hexane to afford **3c** as a white solid (2.60 g, 95%). mp: 74–75 °C; IR (CHCl_3) ν 3534, 1620, 1596, 1514, 1466, 1432, 1387, 1346, 1264, 1201, 1141 cm^{-1} ; ^1H -NMR (CDCl_3) δ : 7.80 (2H, d, J = 8.5 Hz), 7.68 (1H, d, J = 9.1 Hz), 7.66 (1H, s), 7.51 (1H, dt, J = 7.9, 1.2 Hz), 7.42–7.34 (1H, m), 7.17 (1H, d, J = 9.1 Hz), 5.23 (1H, s); ^{13}C NMR (75 MHz, DMSO- d_6) δ 150.0, 132.3, 131.6, 131.0, 129.0, 128.6, 127.3, 124.2, 123.7, 118.0, 115.7, 97.2; HRMS (EI) m/z calcd. for: $[\text{M}]^+$ 325.8940, m/z found: 325.8942.

2-(2,2-Dibromovinyl)-6-methoxyphenol (**3d**)

To a solution of 2-hydroxy-3-methoxy-benzaldehyde (5.0 g, 18.7 mmol) in CH_2Cl_2 (250 mL) was added carbon tetrabromide (9.35 g, 28.2 mmol) and triphenylphosphine (14.7 g, 56.1 mmol) at 0 °C, and the mixture was stirred for 24 h at rt. 1M $\text{Na}_2\text{S}_2\text{O}_3$ (40 mL) was added, and the resulting mixture was extracted with CH_2Cl_2 (2 $\times$ 60 mL). The combined extracts were washed with H_2O and brine, then dried (MgSO_4) and solvent removed under reduced pressure. The residue was purified by flash chromatography eluting with 5% EtOAc in hexane to afford *tert*-butyl[2-(2,2-dibromovinyl)-6-methoxyphenoxy]dimethylsilane as a colorless oil (7.50 g, 95%). IR (CHCl_3) ν 2927, 2854, 1576, 1476, 1256, 1229, 1076 cm^{-1} ; ^1H -NMR (CDCl_3) δ : 7.59 (1H, s), 7.24–7.19 (1H, m), 6.89 (1H, d, J = 8.0 Hz), 6.84 (1H, dd, J = 8.0, 1.8 Hz), 3.79 (3H, s), 1.02 (9H, s), 0.17 (6H, s); ^{13}C NMR (75 MHz, DMSO- d_6) δ 150.4, 142.6, 134.3, 127.9, 120.8 (2C), 111.8, 90.0, 55.1, 25.9, 18.7, -4.2; HRMS (EI) m/z calcd. for: $[\text{M}-t\text{Bu}]^+$ 362.9052, m/z found: 362.9047.

To a solution of *tert*-butyl[2-(2,2-dibromovinyl)-6-methoxyphenoxy]dimethylsilane (7.5 g, 17.7 mmol) in THF (80 mL) was added TBAF (26 mL, 26.0 mmol) at 0 °C, and the mixture was stirred for 3 h at rt. This mixture was then concentrated on a rotary evaporator to approximately 40 mL. Water (20 mL) was added, and the resulting mixture was extracted with EtOAc (2 $\times$ 60 mL). The combined extracts were washed with sat.

NH₄Cl and brine, then dried (MgSO₄) and solvent was removed under reduced pressure. The residue was purified by flash chromatography eluting with 20% EtOAc in hexane to afford **3d** as a white solid (4.42 g, 81%). mp: 43-44 °C; IR (CHCl₃) ν 3504, 2935, 2837, 1613, 1473, 1359, 1258, 1068 cm⁻¹; ¹H-NMR (CDCl₃) δ : 7.65 (1H, s), 7.38-7.30 (1H, m), 6.89-6.82 (2H, m), 5.85 (1H, s), 3.90 (3H, s); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 146.6, 143.5, 132.1, 122.0, 120.9, 119.4, 110.8, 90.3, 56.3; HRMS (EI) *m/z* *calcd.* for: [M]⁺ 305.8891, *m/z* *found*: 305.8898.

II. Benzofurans (4)

2-Oct-1-ynylbenzofuran (4a)

A carousel reaction tube (24×150 mm) was charged with 2-(2,2-dibromovinyl)phenol (115 mg, 0.41 mmol), 10% Pd-C (4.4 mg, 0.0041 mmol, 1 mol%), P(*p*-MeOPh)₃ (5.8 mg, 0.017 mmol, 4 mol%), and CuI (1.6 mg, 0.0083 mmol, 2 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (2 mL, degassed), H₂O (1 mL, degassed), *i*Pr₂NH (145 μ L, 1.03 mmol) and 3-ethynylpyridine (83 μ L, 0.75 mmol), and then heated to 100 °C with stirring for 12 h. The reaction mixture was then cooled to rt and H₂O (10 mL) added. The mixture was extracted with EtOAc (2 $\times$ 15 mL), and combined extracts were washed with sat. NH₄Cl and brine, then dried and solvent was removed *in vacuo*. The resulting crude material was purified by flash chromatography eluting with 2% EtOAc in hexane to afford **4a** as a white solid (74.5 mg, 80%). IR (CHCl₃) ν 2927, 2855, 2230, 1567, 1448, 1349, 1304, 1253, 1196, 1156, 1141, 1107, 1009 cm⁻¹; ¹H-NMR (CDCl₃) δ : 7.55-7.49 (1H, m), 7.45-7.40 (1H, m), 7.33-7.18 (2H, m), 6.81 (1H, s), 2.48 (2H, t, *J* = 7.0 Hz), 1.71-1.24 (8H, m), 0.91 (3H, t, *J* = 6.9 Hz); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 139.5, 125.2, 123.2, 121.1, 111.2, 110.2, 97.3, 71.4, 31.5, 28.8, 28.4, 22.7, 19.8, 14.2; HRMS (EI) *m/z* *calcd.* for: [M]⁺ 226.1358, *m/z* *found*: 226.1356.

Benzofuran-2-ylethynyltrimethylsilane (4b)

A carousel reaction tube (24×150 mm) was charged with 2-(2,2-dibromovinyl)phenol

(140 mg, 0.50 mmol), 10% Pd-C (10.6 mg, 0.01 mmol, 1 mol%), P(*p*-MeOPh)₃ (7.1 mg, 0.02 mmol, 4 mol%), and CuI (1.9 mg, 0.010 mmol, 2 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (3 mL, degassed), *i*Pr₂NH (180 μL, 1.28 mmol) and trimethylsilylacetylene (0.71 mL, 5.0 mmol), and then heated to 100 °C with stirring for 12 h. The reaction mixture was then cooled to rt and H₂O (10 mL) added. The mixture was extracted with EtOAc (2 × 15 mL), and combined extracts were washed with sat. NH₄Cl and brine, then dried and solvent was removed *in vacuo*. The resulting crude material was purified by flash chromatography eluting with 0.2% EtOAc in hexane to afford **4b** as a colorless oil (50.0 mg, 47%). IR (CHCl₃) ν 2960, 2900, 2160, 1557, 1448, 1413, 1352, 1307, 1252, 1181, 1108, 1010 cm⁻¹; ¹H-NMR (CDCl₃) δ : 7.25 (1H, d, *J* = 7.6 Hz), 7.14 (1H, d, *J* = 8.5 Hz), 7.07-6.90 (2H, m), 6.65 (1H, s), 0.03 (9H, t, *J* = 11.7 Hz); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 155.0, 138.8, 127.7, 126.1, 123.6, 121.6, 112.3, 111.6, 102.2, 94.6, 0.0; HRMS (EI) *m/z* calcd. for: [M]⁺ 214.0814, *m/z* found: 214.0820.

(3-Benzofuran-2-yl)prop-2-yn-1-ol (**4c**)

A carousel reaction tube (24×150 mm) was charged with 2-(2,2-dibromovinyl)phenol (120 mg, 0.43 mmol), 10% Pd-C (4.6 mg, 0.0043 mmol, 1 mol%), P(*p*-MeOPh)₃ (6.0 mg, 0.017 mmol, 4 mol%), and CuI (1.6 mg, 0.0086 mmol, 2 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (2 mL, degassed), H₂O (1 mL, degassed), *i*Pr₂NH (157 μL, 1.12 mmol) and propargyl alcohol (0.10 mL, 1.30 mmol), and then heated to 100 °C with stirring for 12 h. The reaction mixture was then cooled to rt and H₂O (10 mL) added. The mixture was extracted with EtOAc (2 × 15 mL), and combined extracts were washed with sat. NH₄Cl and brine, then dried and solvent was removed *in vacuo*. The resulting crude material was purified by flash chromatography eluting with 33% EtOAc in hexane to afford **4c** as a colorless oil (36.0 mg, 49%). IR (CHCl₃) ν 3350, 2224, 1566, 1448, 1349, 1306, 1265, 1189, 1157, 1141, 1108, 1027 cm⁻¹; ¹H-NMR (CDCl₃) δ : 7.55 (1H, d, *J* = 7.6 Hz), 7.45 (1H, d, *J* = 7.3 Hz), 7.38-7.20 (2H, m), 6.95 (1H, s), 4.56 (2H, d, *J* = 6.0 Hz), 1.80 (1H, t, *J* = 6.0 Hz); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 155.0, 137.9, 127.6, 125.9, 123.5, 121.5, 112.2, 111.5, 93.5, 76.5, 51.7; HRMS (EI) *m/z* calcd. for: [M]⁺ 172.0532, *m/z* found: 172.0524.

[(3-Benzofuran-2-yl)prop-2-ynyloxy]-*tert*-butyldiphenylsilane (4d)

A carousel reaction tube (24×150 mm) was charged with 2-(2,2-dibromovinyl)phenol (140 mg, 0.50 mmol), 10% Pd-C (5.3 mg, 0.0050 mmol, 1 mol%), P(*p*-MeOPh)₃ (7.1 mg, 0.020 mmol, 4 mol%), and CuI (1.9 mg, 0.010 mmol, 2 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (2 mL, degassed), H₂O (1 mL, degassed), *i*Pr₂NH (175 μL, 1.25 mmol) and *tert*-butyldiphenylprop-2-ynyloxysilane (221 mg, 0.75 mmol), and then heated to 100 °C with stirring for 12 h. The reaction mixture was then cooled to rt and H₂O (10 mL) added. The mixture was extracted with EtOAc (2 × 15 mL), and combined extracts were washed with sat. NH₄Cl and brine, then dried and solvent was removed *in vacuo*. The resulting crude material was purified by flash chromatography eluting with 4% EtOAc in hexane to afford **4d** as a colorless oil (165 mg, 80%). IR (CHCl₃) ν 3071, 2931, 2857, 1589, 1568, 1471, 1463, 1450, 1428, 1372, 1255, 1191, 1113 cm⁻¹; ¹H-NMR (CDCl₃) δ : 7.78-7.72 (4H, m), 7.57-7.20 (10H, m), 6.86 (1H, d, *J* = 0.6 Hz), 4.58 (2H, s), 1.09 (9H, s); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 154.7, 138.3, 135.6, 132.8, 129.9, 127.8, 127.5, 125.5, 123.2, 121.1, 111.7, 111.2, 93.7, 75.5, 53.0, 26.7, 19.2; HRMS (EI) *m/z* *calcd.* for: [M]⁺ 410.1702, *m/z* *found*: 410.1704.

(4-Benzofuran-2-yl)but-3-yn-1-ol (4e)

A carousel reaction tube (24×150 mm) was charged with 2-(2,2-dibromovinyl)phenol (120 mg, 0.43 mmol), 10% Pd-C (4.6 mg, 0.0043 mmol, 1 mol%), P(*p*-MeOPh)₃ (6.0 mg, 0.017 mmol, 4 mol%), and CuI (1.6 mg, 0.0086 mmol, 2 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (2 mL, degassed), H₂O (1 mL, degassed), *i*Pr₂NH (157 μL, 1.12 mmol) and 3-butyn-1-ol (50 μL, 0.65 mmol), and then heated to 100 °C with stirring for 12 h. The reaction mixture was then cooled to rt and H₂O (10 mL) added. The mixture was extracted with EtOAc (2 × 15 mL), and combined extracts were washed with sat. NH₄Cl and brine, then dried and solvent was removed *in vacuo*. The resulting crude material was purified by flash chromatography eluting with 20%–30% EtOAc in hexane to afford **4e** as a pale yellow oil (50.6 mg, 63%). IR (CHCl₃) ν 3376, 2886, 2234, 1566, 1471, 1448, 1350, 1304, 1253, 1190, 1158, 1141, 1108, 1043, 1010 cm⁻¹; ¹H-NMR (CDCl₃) δ : 7.54 (1H, d, *J* = 8.4 Hz), 7.43 (1H, d, *J* = 8.4 Hz), 7.35-7.19 (2H, m), 6.87 (1H, s), 3.87 (2H, q, *J* = 6.3

Hz), 2.78 (2H, t, $J = 6.3$ Hz), 1.80 (1H, t, $J = 6.3$ Hz); ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ 154.7, 138.8, 127.8, 125.6, 123.4, 121.3, 111.3, 111.0, 93.4, 73.2, 60.9, 24.2; HRMS (EI) m/z calcd. for: $[\text{M}]^+$ 186.0685, m/z found: 186.0681.

(6-Benzofuran-2-yl)hex-5-ynenitrile (4f)

A carousel reaction tube (24×150 mm) was charged with 2-(2,2-dibromovinyl)phenol (120 mg, 0.43 mmol), 10% Pd-C (4.6 mg, 0.0043 mmol, 1 mol%), $\text{P}(p\text{-MeOPh})_3$ (6.1 mg, 0.017 mmol, 4 mol%), and CuI (1.7 mg, 0.0086 mmol, 2 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (2 mL, degassed), H_2O (1 mL, degassed), $i\text{Pr}_2\text{NH}$ (160 μL , 1.18 mmol) and 5-hexynenitrile (70 μL , 0.65 mmol), and then heated to 100 $^\circ\text{C}$ with stirring for 12 h. The reaction mixture was then cooled to rt and H_2O (10 mL) added. The mixture was extracted with EtOAc (2 × 15 mL), and combined extracts were washed with sat. NH_4Cl and brine, then dried and solvent was removed *in vacuo*. The resulting crude material was purified by flash chromatography eluting with 15% EtOAc in hexane to afford **4f** as a colorless oil (68.5 mg, 76%). IR (CHCl_3) ν 3061, 2945, 2246, 1732, 1568, 1450, 1428, 1351, 1306, 1253, 1199, 1158, 1142, 1109, 1010 cm^{-1} ; ^1H -NMR (CDCl_3) δ : 7.54 (1H, d, $J = 7.6$ Hz), 7.44 (1H, d, $J = 8.2$ Hz), 7.37-7.20 (2H, m), 6.87 (1H, s), 2.70 (2H, t, $J = 6.9$ Hz), 2.58 (2H, t, $J = 6.9$ Hz), 2.03 (2H, q, $J = 6.9$ Hz); ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ 154.8, 138.6, 127.7, 125.7, 123.4, 121.3, 119.1, 111.3, 111.2, 93.6, 73.3, 24.4, 18.9, 16.5; HRMS (EI) m/z calcd. for: $[\text{M}]^+$ 209.0841, m/z found: 209.0839.

(2-Phenylethynyl)benzofuran (4g)

A carousel reaction tube (24×150 mm) was charged with 2-(2,2-dibromovinyl)phenol (139 mg, 0.50 mmol), 10% Pd-C (5.3 mg, 0.0043 mmol, 1 mol%), $\text{P}(p\text{-MeOPh})_3$ (7.1 mg, 0.020 mmol, 4 mol%), and CuI (2.0 mg, 0.010 mmol, 2 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (3 mL, degassed), $i\text{Pr}_2\text{NH}$ (176 μL , 1.25 mmol) and phenylacetylene (83 μL , 0.75 mmol), and then heated to 100 $^\circ\text{C}$ with stirring for 12 h. The reaction mixture was then cooled to rt and H_2O (10 mL) added. The mixture was extracted with EtOAc (2 × 15 mL), and combined extracts were washed with sat. NH_4Cl and brine, then dried and solvent was removed *in vacuo*.

The resulting crude material was purified by flash chromatography eluting with 1% EtOAc in hexane to afford **4g** as a white solid (77.7 mg, 71%). mp: 71-72 °C; IR (CHCl₃) ν 2926, 2857, 1595, 1499, 1450, 1377, 1313 cm⁻¹; ¹H-NMR (CDCl₃) δ : 7.62-7.55 (3H, m), 7.48 (1H, d, *J* = 7.9 Hz), 7.42-7.23 (5H, m), 7.02 (1H, s); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 154.9, 138.7, 131.6, 129.1, 128.5, 127.7, 125.6, 123.3, 121.8, 121.2, 111.6, 111.2, 95.0, 79.6; HRMS (EI) *m/z* calcd. for: [M]⁺ 218.0732, *m/z* found: 218.0732.

3-Benzofuran-2-ylethynyl-pyridine (4h)

A carousel reaction tube (24×150 mm) was charged with 2-(2,2-dibromovinyl)phenol (139 mg, 0.50 mmol), 10% Pd-C (5.3 mg, 0.0043 mmol, 1 mol%), P(*p*-MeOPh)₃ (7.1 mg, 0.020 mmol, 4 mol%), and CuI (2.0 mg, 0.010 mmol, 2 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (3 mL, degassed), *i*Pr₂NH (180 μ L, 1.28 mmol) and 3-ethynylpyridine (77.8 mg, 0.75 mmol), and then heated to 100 °C with stirring for 12 h. The reaction mixture was then cooled to rt and H₂O (10 mL) added. The mixture was extracted with EtOAc (2 × 15 mL), and combined extracts were washed with sat. NH₄Cl and brine, then dried and solvent was removed *in vacuo*. The resulting crude material was purified by flash chromatography eluting with 25% 30% EtOAc in hexane to afford **4h** as a white solid (67.3 mg, 61%). mp: 75-76 °C; IR (CHCl₃) ν 2357, 1558, 1506, 1472, 1447, 1407, 1257, 1169, 947 cm⁻¹; ¹H-NMR (CDCl₃) δ : 8.83 (1H, s), 8.60 (1H, s), 7.86 (1H, dt, *J* = 7.9, 1.8 Hz), 7.60 (1H, d, *J* = 7.6 Hz), 7.49 (1H, d, *J* = 8.2 Hz), 7.40-7.23 (3H, m), 7.07 (1H, s); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 155.2, 152.4, 149.5, 138.6, 127.7, 126.2, 123.6, 123.3, 121.6, 112.7, 111.5, 91.8, 83.1; HRMS (EI) *m/z* calcd. for: [M]⁺ 219.0684, *m/z* found: 219.0683.

(8*R*,9*S*,13*S*,14*S*,17*S*)-17-Benzofuran-2-ylethynyl-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthrene-3,17-diol (4i)

A carousel reaction tube (24×150 mm) was charged with 2-(2,2-dibromovinyl)phenol (100 mg, 0.36 mmol), 10% Pd-C (3.8 mg, 0.0036 mmol, 1 mol%), P(*p*-MeOPh)₃ (5.1 mg, 0.014 mmol, 4 mol%), and CuI (1.4 mg, 0.0072 mmol, 2 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (2 mL, degassed), H₂O (1 mL, degassed), *i*Pr₂NH (180 μL, 1.28 mmol) and 17- α -ethynylestradiol (148 mg, 0.54 mmol), and then heated to 100 °C with stirring for 12 h. The reaction mixture was then cooled to rt and H₂O (10 mL) added. The mixture was extracted with EtOAc (2 × 15 mL), and combined extracts were washed with sat. NH₄Cl and brine, then dried and solvent was removed *in vacuo*. The resulting crude material was purified by flash chromatography eluting with 35%–40% EtOAc in hexane to afford **4i** as a white solid (102.0 mg, 69%). mp: 208–210 °C; IR (CHCl₃) ν 3378, 3017, 2913, 2398, 1578, 1493, 1436, 1358, 1216, 1134, 1108, 1059, 1006 cm⁻¹; ¹H-NMR (DMSO-*d*₆) δ : 8.98 (1H, s), 7.61 (1H, d, *J* = 7.0 Hz), 7.55 (1H, d, *J* = 8.5 Hz), 7.39–7.19 (3H, m), 7.05 (1H, d, *J* = 8.5 Hz), 6.50 (1H, dd, *J* = 8.4, 2.4 Hz), 6.42 (1H, d, *J* = 2.4 Hz), 5.74 (1H, s), 2.70 (2H, s), 2.38–2.18 (2H, m), 2.15–1.90 (2H, m), 1.86–1.56 (5H, m), 1.48–1.16 (4H, m), 0.92 (3H, s); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 155.6, 154.7, 138.6, 137.8, 130.8, 127.9, 126.8, 126.4, 124.1, 122.0, 115.6, 113.4, 111.9, 111.7, 101.9, 79.5, 75.5, 50.2, 48.0, 43.9, 33.6, 29.8, 27.6, 26.8, 23.3, 13.5; HRMS (EI) *m/z* *calcd.* for: [M]⁺ 412.2048, *m/z* *found*: 412.2038; *Anal. calcd.* for C₂₈H₂₈O₃·0.25H₂O: C 80.64, H 6.89, *found*: C 80.94, H 6.75.

2-Oct-1-ynyl-benzofuran-5-carboxylic acid methyl ester (**4j**)

A carousel reaction tube (24×150 mm) was charged with 3-(2,2-dibromovinyl)-4-hydroxybenzoic acid methyl ester (105 mg, 0.31 mmol), 10% Pd-C (6.6 mg, 0.0062 mmol, 2 mol%), P(*p*-MeOPh)₃ (8.8 mg, 0.025 mmol, 8 mol%), and CuI (2.4 mg, 0.013 mmol, 4 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (2 mL, degassed), H₂O (1 mL, degassed), *i*Pr₂NH (123 μL, 0.875 mmol) and 1-octyne (70 μL, 0.47 mmol), and then heated to 100 °C with stirring for 12 h. The reaction mixture was then cooled to rt and H₂O (10 mL) added. The mixture was extracted with EtOAc (2 × 15 mL), and combined extracts were washed with sat. NH₄Cl and brine, then dried and solvent was removed *in vacuo*. The resulting crude material was purified by flash chromatography eluting with 3% EtOAc in hexane to afford **4j** as a colorless oil (82.4 mg, 93%). IR (CHCl₃) ν 2929, 2234, 1732, 1615, 1574, 1435, 1348, 1311, 1197, 1148, 1116, 1087 cm⁻¹; ¹H-NMR (CDCl₃) δ : 8.26 (1H, d, *J* = 1.5 Hz), 8.02

(1H, dd, $J = 8.8, 1.8$ Hz), 7.44 (1H, d, $J = 8.5$ Hz), 6.86 (1H, s), 3.93 (3H, s), 2.49 (2H, t, $J = 7.2$ Hz), 1.71-1.24 (8H, m), 0.91 (3H, t, $J = 6.9$ Hz); ^{13}C NMR (75 MHz, DMSO- d_6) δ 167.3, 157.1, 140.9, 128.1, 126.9, 125.7, 123.6, 111.1, 110.4, 98.2, 70.9, 52.3, 31.5, 28.8, 28.3, 22.7, 19.8, 14.2; HRMS (EI) m/z calcd. for: $[\text{M}]^+$ 284.1416, m/z found: 284.1412.

2-Oct-1-ynynaphtho[2,1-*b*]furan (4k)

A carousel reaction tube (24×150 mm) was charged with 1-(2,2-dibromovinyl)naphthalen-2-ol (135 mg, 0.41 mmol), 10% Pd-C (4.4 mg, 0.0041 mmol, 1 mol%), $\text{P}(p\text{-MeOPh})_3$ (5.8 mg, 0.016 mmol, 4 mol%), and CuI (1.7 mg, 0.0082 mmol, 2 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (2 mL, degassed), H_2O (1 mL, degassed), $i\text{Pr}_2\text{NH}$ (145 μL , 1.03 mmol) and 1-octyne (100 μL , 0.66 mmol), and then heated to 100 $^\circ\text{C}$ with stirring for 12 h. The reaction mixture was then cooled to rt and H_2O (10 mL) added. The mixture was extracted with EtOAc (2 × 15 mL), and combined extracts were washed with sat. NH_4Cl and brine, then dried and solvent was removed *in vacuo*. The resulting crude material was purified by flash chromatography eluting with 0.8% EtOAc in hexane to afford **4k** as a colorless oil (112.0 mg, 98%). IR (CHCl_3) ν 3056, 2930, 2857, 2233, 1629, 1556, 1524, 1455, 1386, 1344, 1326, 1292, 1236, 1218, 1158, 1135, 1079 cm^{-1} ; ^1H -NMR (CDCl_3) δ : 8.06 (1H, d, $J = 8.2$ Hz), 7.90 (1H, d, $J = 8.2$ Hz), 7.71 (1H, d, $J = 9.1$ Hz), 7.61-7.43 (3H, m), 7.30 (1H, s), 2.51 (2H, t, $J = 7.0$ Hz), 1.72-1.23 (8H, m), 0.91 (3H, t, $J = 6.3$ Hz); ^{13}C NMR (75 MHz, DMSO- d_6) δ 152.3, 138.9, 130.6, 128.9, 127.5, 126.7, 126.3, 124.9, 123.6, 123.3, 112.3, 109.3, 97.3, 71.6, 31.5, 28.8, 28.5, 22.7, 19.9, 14.3; HRMS (EI) m/z calcd. for: $[\text{M}]^+$ 276.1505, m/z found: 276.1514.

7-Methoxy-2-oct-1-ynylbenzofuran (4l)

A carousel reaction tube (24×150 mm) was charged with 2-(2,2-dibromovinyl)-6-methoxyphenol (120 mg, 0.39 mmol), 10% Pd-C (29.0 mg, 0.027 mmol, 7 mol%), $\text{P}(p\text{-MeOPh})_3$ (13.7 mg, 0.039 mmol, 10 mol%), and CuI (3.7

mg, 0.020 mmol, 5 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (2 mL, degassed), H₂O (1 mL, degassed), *i*Pr₂NH (164 μ L, 1.17 mmol) and 1-octyne (86 μ L, 0.58 mmol), and then heated to 100 °C with stirring for 64 h. The reaction mixture was then cooled to rt and H₂O (10 mL) added. The mixture was extracted with EtOAc (2 $\times$ 15 mL), and combined extracts were washed with sat. NH₄Cl and brine, then dried and solvent was removed *in vacuo*. The resulting crude material was purified by flash chromatography eluting with 2% EtOAc in hexane to afford **4l** as a pale yellow oil (80.0 mg, 80%). IR (CHCl₃) ν 2934, 2857, 2234, 1621, 1615, 1593, 1494, 1489, 1455, 1435, 1359, 1318, 1270, 1210, 1183, 1159, 1098, 1061 cm⁻¹; ¹H-NMR (CDCl₃) δ : 7.17-7.08 (2H, m), 6.84-6.74 (2H, m), 4.00 (3H, s), 2.46 (2H, t, *J* = 7.0 Hz), 1.68-1.23 (8H, m), 0.90 (3H, t, *J* = 6.9 Hz). ¹³C NMR (75 MHz, DMSO-*d*₆) δ 145.3, 144.0, 139.7, 129.6, 123.9, 113.4, 110.3, 107.3, 97.1, 71.2, 56.3, 31.5, 28.8, 28.4, 22.7, 19.7, 14.2; HRMS (EI) *m/z* calcd. for: [M]⁺ 256.1468, *m/z* found: 256.1463.

3-Methyl-2-oct-1-ynyl-benzofuran (4m)

A carousel reaction tube (24 $\times$ 150 mm) was charged with 2-(2,2-Dibromo-1-methylvinyl)phenol (145 mg, 0.50 mmol), 10% Pd-C (10.6 mg, 0.010 mmol, 2 mol%), P(*p*-MeOPh)₃ (13.9 mg, 0.040 mmol, 8 mol%), and CuI (4.0 mg, 0.022 mmol, 4 mol%), and was evacuated and purged with argon three times. To this mixture were added toluene (2 mL, degassed), H₂O (1 mL, degassed), *i*Pr₂NH (210 μ L, 1.49 mmol) and 1-octyne (100 μ L, 0.66 mmol), and then heated to 100 °C with stirring for 12 h. The reaction mixture was then cooled to rt and H₂O (10 mL) added. The mixture was extracted with EtOAc (2 $\times$ 15 mL), and combined extracts were washed with sat. NH₄Cl and brine, then dried and solvent was removed *in vacuo*. The resulting crude material was purified by flash chromatography eluting with 0.5%–1.0% EtOAc in hexane to afford **4m** as a colorless oil (98.4 mg, 82%). IR (CHCl₃) ν 2927, 2857, 2228, 1995, 1586, 1451, 1360, 1348, 1256, 1197, 1115, 1094 cm⁻¹; ¹H-NMR (CDCl₃) δ : 7.48-7.43 (1H, m), 7.40-7.35 (1H, m), 7.29 (1H, dt, *J* = 7.3, 1.5 Hz), 7.21 (1H, dt, *J* = 7.3, 1.2 Hz), 2.52 (2H, t, *J* = 7.2 Hz), 2.28 (3H, s), 1.72-1.59 (2H, m), 1.55-1.21 (6H, m), 0.91 (3H, t, *J* = 6.9 Hz); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 154.2, 136.6, 129.2, 125.2, 122.7, 119.6 (2C), 111.2, 99.4, 70.8, 31.5, 28.8, 28.6, 22.7, 19.9, 14.2, 8.9; HRMS (EI) *m/z* calcd. for: [M]⁺ 240.1514, *m/z* found: 240.1508.

Spectra

Indoles

D:\NMR file\20060707-mm020704a\Proton-001.fid

D:\NMR file\20060706-mm020704a\2nd-001.fid

D:\NMR\data\20060728-mm021505-Proton-001.fid

D:\NMR\data\20060728-mm021504-2pxi-001.fid

D:\NMR\data\20060823-mm022501a-Proton-001.fid

D:\NMR\data\20060824-mm022501a-13C-001.fid

E:\Documents and Settings\delusa\My Documents\7204-Hals

D:\NMR\data\20060620-mmD4-7204a-2p-004.fid

Benzofurans

D:\NMR\data\20060916-mm045101a-Proton-001.fid

D:\NMR\data\20060916-mm045101a-2pu-001.fid

D:37NM.R 637200605D4-mm014001a-Proton-001.fid

D:37NM.R 637200605D4-mm014001a-2001-001.fid

D:\NMR file\20060502-mm013904a-Proton-001.fid

D:\NMR file\20060502-mm013904a-2p01-001.fid

0-37NM R f d 20060718-mm021204_Protoc-001.fid 3rd

0-37NM R f d 20060718-mm021204_s2prot-001.fid 3rd